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by

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**Oxo Complexes of Tungstenocene via Oxidation of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{OCH}_3)(\text{CH}_3)]$ and
Related Reactions: Synthesis, Structural Characterization, and Photodisproportionation of
the Spin Paired $d^1\text{-}d^1$ Oxo Bridged Dimer $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})]^{2+}$ and Synthesis
and Characterization of the d^0 Terminal Oxo Complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]^+$**

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Prepared for Publication in Organometallics

Abstract. Oxidation of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{OCH}_3)(\text{CH}_3)]$ (**1**) with ferrocenium hexafluorophosphate in wet methyl ethyl ketone at room temperature leads to a 78% yield of a W(V) oxo complex $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{OCH}_3)\}_2(\mu\text{-O})]^{2+}$ (**2²⁺**), established by a single crystal X-ray diffraction study of the PF_6^- salt (**2**) $[\text{PF}_6]_2$ - monoclinic space group $\text{P2}_1/\text{c}$, $a = 7.246(3)$, $b = 18.796(6)$, $c = 9.438(4)$ Å, $\beta = 89.98(2)^\circ$, $d_c = 2.49 \text{ g mL}^{-1}$, $Z = R_w = 3.09\%$) to contain two d^1 $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)]^{2+}$ moieties connected by a linear oxo bridge such that the W atoms, the bridging oxo, and the methyl groups are coplanar with an anti orientation of the methyl groups. The molecule is diamagnetic in the solid state and in solution as a consequence of spin pairing of the metal centers through a π -interaction involving the oxo bridge, and exhibits a strong absorption in the visible ($\lambda_{\text{max}} = 525 \text{ nm}$, $\epsilon = 23,600 \text{ L mole}^{-1}\text{cm}^{-1}$) assigned to a transition with some MLCT character from a non-bonding level formed by the π -interaction to an empty antibonding level with π^* character. The oxo bridged dimer **2²⁺** is photosensitive, and photodisproportionates in CH_3CN to give the d^0 terminal oxo complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]^+$ (**3⁺**) and the d^2 solvent trapped methyl complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{NCCH}_3)(\text{CH}_3)]^+$ (**4⁺**). The W(IV) acetonitrile complex **4⁺** has been independently isolated and characterized following protolysis of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$ (**7**) with $\text{NH}_4 \text{PF}_6$ in CH_3CN . The W(VI) oxo complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)] \text{PF}_6$ (**3PF₆**) has been prepared in 74% yield by photolysis of **4PF₆** in acetone under O_2 . An X-ray diffraction study of the I^- salt **3I** (cubic space group $\text{Ia}\bar{3}$, $a = b = c = 26.601(4)$ Å, $d_c = 2.53 \text{ g mL}^{-1}$, $Z = 48$, $R_w = 6.03\%$) has established that **3⁺** is a terminal oxo complex. The oxo complex is not formed in the absence of O_2 , even when **4PF₆** is heated in the presence of water, and it is proposed that **3⁺** is formed via addition of O_2 to transient $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)]^+$ to form a reactive peroxo intermediate $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)(\eta^2\text{-O}_2)]^+$. Photolysis of **2PF₆** in the non-coordinating solvent acetone under O_2 results in clean conversion to **3⁺**, by a sequence presumed to involve photodisproportionation of **2²⁺** to give some **3⁺** directly together with $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)]^+$ which is then oxidized to **3⁺**. Ferrocenium oxidation of **1** in CH_2Cl_2 results in formation of the radical cation $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}]^+$, independently prepared and characterized as a PF_6^- salt by ferrocenium oxidation of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}]$, which is in turn prepared by protolysis of **7** with NH_4Cl .

Introduction

There has been remarkable growth throughout the 1980s in the chemistry of transition metal oxo complexes.¹ Interest in what had been regarded as a mature area was rekindled in part by the recognition of the role of the oxo functionality as a "spectator" ligand in catalytic alkene metathesis,² and has been fueled by developments in the chemistry of transition metal porphyrin oxo complexes³ (including their roles in hydrocarbon oxidations and in alkene epoxidation and hydroxylation reactions), by continuing rapid evolution of our understanding of biologically relevant oxo transfer reactions,⁴ by extraordinary advances in the use of oxo complexes as catalysts for alkene hydroxylation⁵ and epoxidation,⁶ and, most recently, by the remarkable catalytic activity demonstrated by high valent rhenium oxo alkyls.⁷ These developments have been paralleled by significant advances in the syntheses of oxo complexes, including the preparations of "low valent" oxo complexes⁸ and of high valent oxo alkyl complexes,^{7,9} and marked extensions of the rational synthesis of organometallic oxo complexes.¹⁰

Our own interest in oxo alkyl complexes began with the modest observation that, although most tungstenocene complexes (with the most notable exception of the dihalides¹¹) are relatively weakly colored, we sometimes observed the formation of traces of hard to isolate purple complexes which we suspected arose from the presence of adventitious oxygen. We had an opportunity to determine whether these were indeed oxo complexes when we discovered that ferrocenium oxidation of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{OCH}_3)(\text{CH}_3)]^{12}$ (**1**) in wet methyl ethyl ketone (MEK) results in the formation of a red-purple crystalline material in good yield. We now wish to report that this material is an oxo complex in which the chromophore is the $d^1\text{-}d^1$ linear oxo bridge within the diamagnetic $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2(\mu\text{-O})]^{2+}$ (**2**²⁺) cation. The most distinctive feature of the chemistry of this complex is the facility with which it photodisproportionates in CH_3CN to give the W(VI) oxo complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]^+$ (**3**⁺) and the W(IV) acetonitrile complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{NCCH}_3)(\text{CH}_3)]^+$ (**4**⁺). Both **3**⁺ and **4**⁺ have been independently prepared as shown in Scheme I, which summarizes the major synthetic observations to be reported.

Experimental Section

General Data. All transformations and manipulations involving air-sensitive compounds were performed using either standard Schlenk techniques or a Vacuum Atmospheres drybox under an atmosphere of prepurified nitrogen unless otherwise noted. Glassware was flame dried under vacuum or dried in an oven (> 4 hr, 120°C) before use.

Solvents and Reagents. Tetrahydrofuran (THF) and diethyl ether were predried over sodium wire and then distilled from sodium/benzophenone ketyl under nitrogen. Ligroine (90-120°C boiling range, Mallinckrodt) was dried over sodium wire before use. Reagent grade acetone (Mallinckrodt) and benzene (Mallinckrodt) were used as received. Toluene was predried over sodium wire and distilled from CaH_2 under nitrogen. Methyl ethyl ketone (MEK - Eastman Kodak) and acetonitrile (Mallinckrodt) were reagent grade and were used as received. Dichloromethane was distilled from CaH_2 under a CaSO_4 drying tube. Water was deionized. Ammonium chloride (Aldrich), sodium iodide (Aldrich), and ammonium hexafluorophosphate (Aldrich) were used as received. Ferrocenium hexafluorophosphate (FcPF_6) was prepared from ferrocene (Aldrich) by a literature procedure.¹³ Triphenyl methylum hexafluorophosphate (trityl PF_6 - Alfa) was recrystallized twice from CH_3CN that had been distilled from CaH_2 . $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2]$ ¹⁴ and $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{OCH}_3)(\text{CH}_3)]$ ¹² were prepared from $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{H}_2]$ by established procedures.

Spectroscopy and Analysis. ^1H NMR spectra were recorded on a Varian CFT-80 (80 MHz), a Bruker AM-300 (300 MHz), or a Bruker WM-300-WB (300 MHz) NMR spectrometer. Perdeuteroacetone, perdeuteroacetonitrile, perdeuterodimethyl sulfoxide (99.5+ atom%) were purchased from Merck, Sharpe, and Dohme or from Cambridge Isotopes and were used as received. Chemical shifts are reported in δ using the residual proton resonances of the deuterated solvents as internal standards (acetone d_5 - δ 2.04; acetonitrile d_2 - δ 1.93; dimethylsulfoxide d_5 - δ 2.49). ^{13}C NMR spectra were obtained on a Bruker AM-300 (75.5 MHz) or a Bruker WM-300-WB (75.5 MHz) NMR spectrometer. Chemical shifts are reported in δ using the ^{13}C chemical shift of the deuterated solvent as an internal standard (dimethylsulfoxide- d_6 - δ 39.5).

Infrared spectra were obtained as KBr pellets or in Nujol mulls on a Perkin Elmer 683 grating infrared spectrometer, with the 1601 cm^{-1} band of polystyrene as an external reference. Mass spectra were recorded on a Kratis MS-9 spectrometer. Mass spectral patterns which exhibited the W isotope envelope are reported as the values of m/e corresponding to the ion containing ^{184}W . EPR spectra were recorded on a Varian E-109 spectrometer in a $60 \times 10 \times 0.25\text{ mm}$ quartz flat cell, and were calibrated against the sharp line ($g = 2.0036$) of a sample of 2,2-diphenyl-1-picrylhydrazyl (DPPH)¹⁵ in a sealed capillary attended externally to the flat cell. Solid state susceptibilities were determined by the Guoy method on a Bruker Research B-E15 B8 magnet equipped with a Cahn RG electrobalance and a Hewlett Packard model 3465A digital multimeter. The sample holder was a 5 mm borosilicate NMR tube cut to a length of 2 cm and fitted with a plastic cap to which was glued (epoxy) a platinum loop. The sample holder was calibrated with $\text{HgCo}(\text{SCN})_4$. Microanalyses were carried out by Dornis u. Kolbe, Mülheim a. d. Ruhr, Germany.

$[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})][\text{PF}_6]_2$ ($2[\text{PF}_6]_2$). A 0.028 M solution of ferrocenium hexafluorophosphate in methyl ethyl ketone (MEK, 30 mL = 0.84 mmol) was added to a stirred dark orange solution of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{OCH}_3)(\text{CH}_3)]$ (0.30 g, 0.83 mmol) in MEK (30 mL) to give, after 10 minutes, a deep cherry-red solution and a flocculent purple-red precipitate. After 24 hours the precipitate was collected by decantation, washed with MEK ($2 \times 5\text{ mL}$), and dried in vacuo to yield spectroscopically pure $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})][\text{PF}_6]_2$ (0.31 g, 0.32 mmol = 76%) as a dark red-purple powder. The complex could be recrystallized as small red-brown needles (ca. 80% recovery) by slowly concentrating a saturated acetone/toluene solution (v/v 5:1) of the complex under reduced pressure. Analytically pure material was obtained as hexagonal plates by slow vapor diffusion of diethyl ether into a saturated acetone solution of the complex. ^1H NMR (300 MHz, acetonitrile- d_3): δ 6.09 (s, 20H, $4\text{C}_5\text{H}_5$), 0.88 (s, satellites $J_{\text{W-H}} = 4.8\text{ Hz}$, 6H, 2CH_3). ^1H NMR (300 MHz, acetone- d_6): δ (s, 20H, $4\text{C}_5\text{H}_5$), (s, satellites $J_{\text{W-H}} = ?\text{ Hz}$, 2WCH_3). ^{13}C NMR (75.5 MHz, gated decoupled, dimethylsulfoxide- d_6): δ 104.2 (δ , $^1J_{\text{C-H}} =$

185.0 Hz, $4C_5H_5$), 3.89 (q, $^1J_{C-H} = 133.2$ Hz, $2CH_3$). IR (KBr): 3138 ms, 2961 mw, 2900 m, 2812 w, 1440 s, 1431 s, 1420 ms, 1382 m, 1206 m, 1128 w, 1084 m, 1022 m, 850 vs br, 741 ms, 702 m, 552 vs, 409 m, 349 $m\text{ cm}^{-1}$. Anal. Calcd for $C_{22}H_{26}F_{12}P_2OW_2$: C, 27.41; H, 2.72. Found: C, 27.43; H, 2.83.

$[W(\eta^5-C_5H_5)_2(NCCH_3)(CH_3)]PF_6(4PF_6)$. A saturated solution (10 mL, ca 0.1 M, 1 mmol) of NH_4PF_6 in acetonitrile was added to $[W(\eta^5-C_5H_5)_2(CH_3)_2]$ (103 mg, 298 μmol). The mixture was swirled and the resulting clear, red solution was left to stand undisturbed for 30 min at room temperature. The solvent was then removed under reduced pressure (37°) and the orange-brown solid was washed with toluene (3 x 5 mL) and then dried under vacuum (3 h). Acetone and water (10 mL ea.) were added to give an orange solution from which the acetone was removed under reduced pressure to precipitate an orange-brown solid. The orange mother liquor was filtered off and the solid was washed with water (3 x 5 mL) and dried under vacuum (50°C , 1 h) to give $[W(\eta^5-C_5H_5)_2(NCCH_3)(CH_3)]PF_6$ as orange-brown "spaghetti-like" crystals (108 mg, 209 $\mu\text{mol} = 70\%$). A sample of these crystals was unchanged in appearance after exposure to air for 10 min. 1H NMR (300 MHz, acetonitrile- d_3): δ 5.18 (s, 10H, $2C_5H_5$), 2.61 (s, 3H, $NCCH_3$), 0.25 (s, satellites $J_{W-H} = 5.3$ Hz, 3H, W- CH_3). 1H NMR (300 MHz, acetone- d_6): δ 5.38 (s, 10H, $2C_5H_5$); 2.86 (s, 3H, $NCCH_3$); 0.36 (s, satellites $J_{W-H} = 5.6$ Hz, 3H, W CH_3). IR (KBr): 3218 m, 3135 br s, 3005 m, 2947 s, 2900 s, 2853 m, 2823 ms, 2415 br w 2320 vw, 2280 w, 1461 m sh, 1439 s, 1437 s, 1427 s sh, 1420 s, 1385 s, 1368 ms sh, 1218 ms, 1117 m, 1080 br m, 1030 ms, 1019 ms, 998 s, 950 s, 938 br s, 848 vs, 825 br vs, 744 ms, 607 m, 596 m, 554 vs, 484 w, 380 w, 357 m, 349 $m\text{ cm}^{-1}$. Anal. Calcd for $C_{13}H_{16}F_6NPW$: C, 30.31; H, 3.13. Found: C, 30.43; H, 3.25.

$[W(\eta^5-C_5H_5)_2(O)(CH_3)]PF_6(3PF_6)$. A stirred orange solution of $[W(\eta^5-C_5H_5)_2(NCCH_3)(CH_3)]PF_6$ (0.30 g, 0.58 mmol) in acetone (30 mL) was irradiated for one hour under oxygen with a 150 W sunlamp. The yellow solution was filtered to remove a small

amount of a grayish precipitate and the solvent removed under reduced pressure to give spectroscopically pure $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]\text{PF}_6$ as yellow flakes (0.21 g, 4.69 mmol \approx 74%). Analytically pure material could be obtained (ca 68% recovery) by slow concentration of a saturated acetone/toluene solution (v/v 1:2) of the complex. ^1H NMR (300 MHz, acetone- d_6): δ 6.90 (s, 10H, $2\text{C}_5\text{H}_5$), 2.16 (s, satellites $J_{\text{W-H}} = 7.8$ Hz, 3H, WCH_3). ^1H NMR (300 MHz, acetonitrile- d_3): δ 6.58 (s, 10H, $2\text{C}_5\text{H}_5$), 2.16 (s, 3H, satellites $J_{\text{W-H}} = 7.8$ Hz, WCH_3). ^{13}C NMR (75.5 MHz, gated decoupled, dimethylsulfoxide- d_6): δ 113.7 (d, $^1J_{\text{C-H}} = 185.5$ Hz, $2\text{C}_5\text{H}_5$), 5.34 (q, $^1J_{\text{C-H}} = 136.4$ Hz, WCH_3). IR (KBr): 3125 s, 2992 w, 2920 mw, 1456 m, 1428 ms, 1382 m, 1217 w, 1132 mw, 1071 mw, 1032 m, 1009 mw, 850 vs br, 740 m, 551 s, 350 mw br cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{OF}_6\text{PW}$: C, 26.96; H, 2.68. Found: C, 27.04; H, 2.78.

$[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]\text{I}$ (3I). An orange solution of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{NCCH}_3)(\text{CH}_3)]\text{PF}_6$ (0.28 g, 0.54 mmol) in acetone (70 mL) was allowed to stir in air in a well lit laboratory for 24 hr. The resulting pale yellow solution was decreased in volume to ca 20 mL under reduced pressure, filtered and cooled to 0°C . This was added to 5.0 mL of a 0.33 M solution of NaI in acetone (0.25 g, 1.65 mmol) also at 0°C . Swirling precipitated $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]\text{I}$ as spectroscopically pure golden yellow flakes under an orange solution. The flakes were collected by decantation, washed with 0°C acetone (1 x 10 mL) and diethyl ether (2 x 10 mL), and dried in vacuo (0.20 g, 0.42 mmol \approx 78%). Analytically pure material could be obtained in low yield as yellow blocks and needles by slow vapor diffusion of diethyl ether into a saturated acetone solution of the complex. ^1H NMR (300 MHz, acetonitrile- d_3): δ 6.61 (s, 10H, $2\text{C}_5\text{H}_5$), 2.17 (s, 3H, satellites $J_{\text{W-H}} = 7.5$ Hz, WCH_3). ^{13}C NMR (75.5 MHz, gated decoupled, dimethylsulfoxide- d_6): δ 113.6 (d, $^1J_{\text{C-H}} = 185.5$ Hz, $2\text{C}_5\text{H}_5$), 5.36 (q, $^1J_{\text{C-H}} = 136.4$ Hz, WCH_3). IR (KBr): 3100 ms, 3055 s, 2972 w, 2918 w, 1451 m, 1422 s, 1382 mw, 1365 w br, 1260 mw, 1214 mw, 1130 mw, 1079 mw, 1053 mw, 1031 m, 1023 m, 1004 m, 974 mw, 880 sh, 867 vs, 838 s, 798 w, 588 w, 499 w cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{IOW}$: C, 27.99; H, 2.78. Found: C, 27.93; H, 2.79.

[W(η^5 -C₅H₅)₂(CH₃)Cl] (12). A dark red solution of [W(η^5 -C₅H₅)₂(CH₃)₂] (0.63 g, 1.83 mmol) and NH₄Cl (2.0 g, 37.4 mmol) in THF (20 mL) was heated at 56°C for 23 hr. The solvent was removed under reduced pressure and the solid residue extracted with benzene (1 x 25 mL, 3 x 10 mL). Ligroine was then added (50 mL) and the solvent mixture filtered. Slow concentration under reduced pressure to ca 15 mL yielded dark brown crystals of spectroscopically pure [W(η^5 -C₅H₅)₂(CH₃)Cl]. The crystals were collected by decantation, washed with ligroine (0°C, 3 x 10 mL), and dried in vacuo (0.41 g, 1.12 mmol \equiv 61%). Analytically pure material could be obtained as dark brown needles (ca 40% recovery) by slow concentration of a saturated diethyl ether solution of the complex. ¹H NMR (80 MHz, acetone-d₆): δ 4.96 (s, 10H, 2C₅H₅), 0.37 (s, 3H, satellites J_{W-H} = 4.8 Hz, WCH₃). IR (KBr): 3110 m br, 2940 m br, 2885 m, 2820 mw br, 1422 ms, 1385 w, 1360 mw, 1250 w br, 1191 m, 1112 m, 1074 mw, 1063 mw, 1010 ms, 994 ms, 943 m, 872 ms, 837 s, 793 ms, 588 ms, 478 ms, 393 m, 364 ms, 339 ms cm⁻¹. Mass spectrum (molecular ion, ¹⁸⁴W) m/e 364. Anal. Calcd for C₁₁H₁₃ClW: C, 36.24; H, 3.60. Found: C, 36.36; H, 3.58.

[W(η^5 -C₅H₅)₂(CH₃)Cl]PF₆ (11PF₆). A 0.016 M solution of FePF₆ in CH₂Cl₂ (30 mL = 0.48 mmol) was added to a stirred dark orange-red solution of [W(η^5 -C₅H₅)₂(CH₃)Cl] (0.18 g, 0.49 mmol) in CH₂Cl₂ (15 mL). Within 1 minute the solution had lightened to a bright orange and had deposited an orange precipitate. The solvent was removed under reduced pressure and the solid residue triturated with toluene (4 x 30 mL) to yield [W(η^5 -C₅H₅)₂(CH₃)Cl]PF₆ as a spectroscopically pure orange powder after vacuum drying (0.23 g, 0.45 mmol \equiv 92%). Analytically pure material could be obtained as clusters of small orange needles (ca. 80% recovery) via slow concentration of a saturated CH₂Cl₂ solution of the complex. EPR (acetone, 25°C, 9.389 GHz): $\langle g \rangle$ = 2.006 (q, a_{H} = 4.0 G). IR (KBr): 3130 s, 2955 m, 2915 ms, 2856 m, 1440 s, 1428 s, 1382 mw, 1340 w, 1261 w, 1212 w, 1128 mw, 1078 mw, 1030 m, 1017 mw, 980

w br, 924 ms, 850 vs br, 743 m, 552 s, 310 s cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{ClF}_6\text{PW}$: C, 25.93, H, 2.58. Found: C, 25.64; H, 2.64.

Reduction of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}]\text{PF}_6$. An orange solution of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}]\text{PF}_6$ (0.11 g, 0.22 mmol) in acetone (30 mL) was vigorously stirred with a saturated solution of aqueous KOH (30 mL) at room temperature for 1.5 hours. The cherry-red organic layer was decanted off and the solvent removed under reduced pressure to give a brown-red solid. Extraction with CH_2Cl_2 (35 mL) gave a red-orange solution which was filtered. Removal of the solvent under reduced pressure gave an oily brown powder which was shown to be $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}]$ (0.04 g, 0.11 mmol = 50%) by comparison (^1H NMR and mass spectroscopy) with an authentic sample.

X-ray Diffraction Studies of $[\{\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})][\text{PF}_6]_2$ (2** $[\text{PF}_6]_2$) and $[\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]\text{I}$ (**3I**).** Crystals of **2** $[\text{PF}_6]_2$ and **3I** for diffraction studies were obtained by vapor diffusion of diethyl ether into a saturated acetone solution of the complexes. Crystals were mounted in glass capillary tubes and flame sealed under argon. Data were collected on a Nicolet R3 diffractometer using graphite monochromatized Mo $\text{K}\alpha$ radiation (50 kV, 30 mA). Data collection was controlled by the Nicolet P3 program¹⁷ and structures were solved using SHELXTL.¹⁸ Diffractometer data were processed with FOXTAPE, a local modification of the Nicolet program XTAPE. Empirical absorption corrections were performed by the program XEMP (Nicolet) while drawings were generated by the program SNOOPI (part of the Oxford University CHEMGRAF Suite package)¹⁹ or by XPLOT (Nicolet). All molecular calculations were performed with the aid of the program XP (Nicolet). Atomic scattering factors were based on literature values for W²⁰ and on those in the SHELXTL program for other atoms. Weights were taken as $[\sigma^2(\text{F}) + g\text{F}^2]^{-1}$. Crystal data, details of the data collection, and final agreement parameters are summarized in Table I.

After initial examination of rotation photographs the unit cells for $2[\text{PF}_6]_2$ and **3I** were determined to be $\text{P}2_1/\text{c}$ and $\text{I}a3$ respectively through application of both the $\text{P}3$ program and TRACER .²¹ Unit cell dimensions were obtained by a least-squares fit of the angular settings of 25 reflections with $18^\circ < 2\theta < 31^\circ$. No decrease in intensity was observed for the check reflections during data collection. Data were corrected for absorption by an empirical procedure which employed six refined parameters to define a pseudo ellipsoid. Lorentz and polarization corrections were applied to the data.

The structures of $2[\text{PF}_6]_2$ and **3I** were solved using the direct methods program SOLV which located the W atom in 2^{2+} and the W and I atoms in **3I**. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and refined anisotropically. Hydrogen atoms were placed in calculated positions with $r(\text{C-H}) = 0.96\text{\AA}$ and $U_{\text{iso}} = 1.2 U_{\text{equiv}}$. Refinement was continued to convergence by using the blocked-cascade least-squares procedure of SHELXTL . Final difference Fourier syntheses showed only diffuse backgrounds. An inspection of F_o vs F_c values and trends based on $\sin \theta$, Miller index or parity group failed to reveal any systematic errors in the data.

The dication in $2[\text{PF}_6]_2$ resides on an inversion center with the bridging oxygen atom at $(1/2, 1/2, 0)$. The hexafluorophosphate anion is ordered and well behaved. The asymmetric unit of **3I** contains three iodide anions, $\text{I}(1)$, $\text{I}(2)$, and $\text{I}(3)$, at special positions with site occupancy factors of $1/6$, $1/2$, and $1/3$ respectively, together with a molecule of the 3^+ cation in a general position. Final atomic positional parameters for $2[\text{PF}_6]_2$ and **3I** are presented in Tables II and III, and anisotropic thermal parameters are given in Tables SI and SII of the Supplementary Material.

Results and Discussion

The methoxy complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{OCH}_3)(\text{CH}_3)]$ (**1**) is readily prepared from $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)(\text{OCOPh})]$ ²² by reaction with excess NaOCH_3 in CH_3OH ,^{12b} and our interest in the oxidation chemistry of **1** began when we included the complex in an electrochemical study of

one electron oxidation of d^2 tungstenocene derivatives $[W(\eta^5-C_5H_5)_2XY]$.²³ It has been known for many years that such complexes are readily oxidized to give an extensive and remarkably stable class of organometallic radicals containing d^1 $[W(\eta^5-C_5H_5)_2XY]^+$ cations,^{11,22,24,25} but our electrochemical study established that **1** was unique amongst the d^2 tungstenocene substrates examined in exhibiting two electrochemically reversible one electron oxidations at -402 and +431 mV vs SCE respectively. It seemed probable that the products of these oxidations were the 17-electron radical cation $[W(\eta^5-C_5H_5)_2(OCH_3)(CH_3)]^+$ and the formally 16-electron dication $[W(\eta^5-C_5H_5)_2(OCH_3)(CH_3)]^{+2,23}$ and the isolation of either of these complexes would be of interest. H atom abstraction from the methyl group of the monocation could result in an unprecedented insertion of a cationic methyldiene ligand into a metal-oxygen bond,²⁵ while H atom abstraction from the methoxy group of the monocation could give an unusual cationic formaldehyde complex of tungstenocene.²⁶ The dication is also of interest in that no dicationic derivatives of tungstenocene have been previously isolated, and these considerations led us to examine chemical oxidation of $[W(\eta^5-C_5H_5)_2(OCH_3)(CH_3)]$.

Oxidation of $[W(\eta^5-C_5H_5)_2(OCH_3)(CH_3)]$ in Methyl Ethyl Ketone - Formation of $[W(\eta^5-C_5H_5)_2(CH_3)]_2(\mu-O)[PF_6]_2$. Initial oxidation experiments involved the reaction of **1** with the one-electron oxidants ferrocenium hexafluorophosphate ($[Fe(\eta^5-C_5H_5)_2]PF_6$ - $FcPF_6$) and trityl hexafluorophosphate ($[Ph_3C]PF_6$) in CH_2Cl_2 at $-78^\circ C$, conditions which we have previously found convenient for one-electron oxidation of $[W(\eta^5-C_5H_5)_2RR']$ complexes to the corresponding radical cations.²⁵ With **1**, however, these conditions led to the formation of complex mixtures of products (the nature of which will be discussed later) and we turned instead to the use of ketonic solvents, particularly methyl ethyl ketone (MEK). This is the solvent of choice for oxidation of **1** because it is sufficiently polar to dissolve $FcPF_6$, but the primary oxidation product of **1** is insoluble in MEK while the oxidation by products are soluble.

Addition of one equivalent of $FcPF_6$ to an orange MEK solution of $[W(\eta^5-C_5H_5)_2(OCH_3)(CH_3)]$ at room temperature resulted in an immediate reaction, as evidenced by a

solution color change to cherry-red. Within 10 minutes a dark red-purple flocculent solid began to precipitate from the solution. After the reaction mixture had been stirred overnight, the air stable solid was isolated by decantation, washed with a little MEK, and dried under vacuum.

^1H and ^{13}C NMR spectra of the purple solid (CD_3CN) established the presence of the $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)]$ moiety. The material was only soluble in the most polar solvents (acetone, acetonitrile), suggesting an ionic formulation, and IR spectra of a Nujol mull established the presence of the PF_6^- anion. No other functional groups could be readily identified spectroscopically, but it did prove feasible to obtain dark red-purple hexagonal plates of the complex suitable for X-ray diffraction.

Molecular Structure of $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})][\text{PF}_6]_2$. A single crystal X-ray diffraction study of the product of oxidation of **1** in MEK established that the reaction had produced the dimeric W(V) dication $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})]^{2+}$ shown in Figure 1, in which two $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)]^{2+}$ fragments are linked in a centrosymmetric fashion by a bridging oxygen atom such that the methyl groups adopt an anti orientation. Bond lengths and angles within the cation are summarized in Tables IV and V. Combustion analysis data for the diffraction quality crystals are in accord with the formulation of the complex determined by the diffraction study. The ligand geometry about the unique tungsten atom in the dimer is analogous to that found in other $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2]$ systems,²⁷ and consists of a pseudo-tetrahedral arrangement of two slightly staggered η^5 -cyclopentadienyl rings, the bridging oxygen atom, and a methyl group around the tungsten atom. If the two ring centroids, the oxygen atom and the methyl carbon atom are taken to define a distorted tetrahedron, the angles about the tungsten atom display a maximum and minimum deviation from the ideal tetrahedral value (109°) of 21° and 2° , respectively (see Table V).

The tungsten-cyclopentadienyl carbon bond distances are not all equal within experimental error: the distances generally become longer as one moves around the rings away from the methyl group. Within Cp(1) the difference between the longest (W-C(15)) and the

shortest (W-C(13)) distance is 0.085 (12) Å; within Cp(2), the difference between the longest (W-C(25)) and shortest (W-C(22)) distance is 0.082 (12) Å. The average values for the tungsten-cyclopentadienyl carbon bond distances (2.356 (4) Å for Cp(1) and 2.343 (4) for Cp(2)) can be compared with the 2.26 - 2.35 Å range observed for the analogous average distances in other $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2]$ containing complexes.²⁷ The observed deviation in these distances indicates a slight tilting of the cyclopentadienyl rings away from perfect η^5 bonding, which may serve to reduce some of the steric strain introduced by the unsymmetrical ligand environment around the tungsten atom.

The perpendicular distances from the cyclopentadienyl mean ring planes to the tungsten atoms (2.038 Å for Cp(1) and 2.017 Å for Cp(2) and the angle between the ring normals (49.1°) lie just outside the 1.93 - 2.01 Å and 34 - 49° ranges, respectively, observed for the analogous values in other tungstenocene complexes.²⁷

The W(1)-O(1) bond length of 1.904 (0) Å is shorter than the 2.05 - 2.13 Å range observed for the molybdenum-oxygen single bond length in closely related d^2 complexes of molybdenocene²⁸ (the ionic radii of W(V) and Mo(IV) are essentially identical²⁹) and is indicative of some partial double bond character arising from π -interaction between the oxygen p-orbital and the two $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)]^+$ fragment HOMO's (vide infra).

The bridging oxygen atom O(1) sits at the crystallographic center of symmetry at the bridging oxygen atom and the W(1)-O(1)-W(1A) group is therefore exactly linear. The dihedral angle between the plane defined by C(1), W(1), and O(1) and the plane defined by C(1A), W(1A), and O(1) is similarly required to be 180°.

Reduction of $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})]\text{PF}_6$. Although 2^{2+} is not particularly oxygen sensitive (at least in the dark - see below), in sharp contrast with the recently reported isoelectronic niobium complex $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SnMe}_3)_2(\mu\text{-O})\}]$,³⁰ the complex reacts readily under a wide range of reducing conditions including KOH/H₂O/acetone, Li[BET₃Il], Na/Hg and K/benzophenone in THF. These reactions were of considerable interest given the possibility of

reducing 2^{2+} to the unknown d^2 - d^2 dimer "[{W(η^5 -C₅H₅)₂(CH₃)₂(μ -O)]", but no tractable products could be isolated under any of the conditions examined.

Electronic Structure of [W(η^5 -C₅H₅)₂(CH₃)₂(μ -O)]²⁺. The W(V) centers in 2^{2+} are formally d^1 , but the chemical shifts of the cyclopentadienyl and methyl ligands are within normal ranges for a diamagnetic tungstenocene complex and the complex was determined to be diamagnetic in the solid state at room temperature by the Gouy method ($X_m \sim -4.5 \times 10^{-4}$ in cgs units). This observed diamagnetism can be rationalized by invoking the presence of three-center delocalized molecular orbitals formed from the overlap of the singly occupied [W(η^5 -C₅H₅)₂(CH₃)₂]²⁺ fragment HOMO's with a single p-orbital of the bridging oxygen atom (Figure 2).

Spin pairing via the π -interactions in a linear oxo bridge was first invoked by Dunitz and Orgel to explain the diamagnetism of the d^5 - d^5 dimer [Cl₅Ru-O-RuCl₅]⁴⁺,³¹ and the concept was then used by Cotton and coworkers to explain the diamagnetism and conformations of d^1 - d^1 dimer complexes containing linear Mo^V(O)-O-Mo^V(O) linkages.³² These [Mo^V₂O₃]⁴⁺ complexes provide the earliest and best known models in the literature for the molecular and electronic structure of a d^1 - d^1 oxo bridged dimer like 2^{2+} , and Cotton used a simple Hückel molecular orbital treatment to show that, neglecting exchange effects and destabilizing steric repulsions, the interaction between the two d-orbitals and a single oxygen p-orbital (corresponding to a Mo(O_l)(O_b)-Mo(O_l)(O_b) dihedral angle of 0° or 180°) is energetically more favorable than two separate d-p interactions (corresponding to a Mo(O_l)(O_b)-Mo(O_l)(O_b) dihedral angle of 90° and giving rise to a triplet structure).³² Since it is well established that the frontier orbital containing the odd electron in d^1 bent metallocene complexes of the [M(η^5 -C₅H₅)₂XY] type is a mixture of d_{z^2} and $d_{x^2-y^2}$ located within the MXY plane with its major radial extent outside the XMY angle,^{23,34} such a 3-center π -interaction leads, as shown in Figure 2, to the observed structure in which the W atoms, the bridging O, and the methyl groups all lie in a plane with an anti orientation for the methyl groups. The W frontier orbitals and the two

oxygen p-orbitals form a bonding, two non-bonding, and an antibonding orbital, and low spin population of these orbitals leads to a singlet ground state and a W-O bond order of 1.5, consistent with the short W-O bond length.

Similar bonding descriptions have been advanced to account for the diamagnetism of several d^1-d^1 dimers of bent niobocene derivatives established crystallographically to have linear oxo bridges between the Nb(IV) centers.^{10,30} These include $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{n-Bu})\}_2(\mu\text{-O})]$,³⁵ $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}\}_2(\mu\text{-O})]$,³⁶ and $[\{\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Sn-Me}_3)(\mu\text{-O})]$,³⁰ and the structures of these complexes and of 1^{2+} provide an interesting contrast with the structures of d^0-d^0 bent metallocene dimers containing oxo bridges. As summarized in Table VI the d^0-d^0 dimers all have M-O-M' groups which approach linear geometries (reported M-O-M angles range from 165.8 (0)° to 177.0°) and relatively short M-O bonds, characteristics which both suggest significant π -donation of the oxygen non-bonding electrons into the same (but now empty) metallocene frontier orbital in the MXY plane. There is now, however, a dihedral angle of 54 - 77° between the MXO and the M'X'O planes, in sharp contrast with the 180° dihedral angle in the d^1-d^1 cases and consistent with strong π -interactions between the metal centers and both of the oxygen non-bonding electron pairs in orthogonal p-orbitals.

The description of the electronic structure of 2^{2+} embodied in Figure 2 accounts well for the unusual electronic spectrum of 2^{2+} shown in Figure 3. Most tungstenocene complexes are d^0 , d^1 or d^2 systems with yellow, orange or red colors arising from strong UV absorptions with tails in the visible or relatively weak, high energy visible absorptions, unless the complexes contain halide ligands, in which case they are much more intensely colored (often green) probably as a consequence of LMCT absorptions in the visible. Complex 2^{2+} is, however, unique in having a spectrum dominated by a very strong visible absorption at 525 nm ($\epsilon = 23,600 \text{ L mole}^{-1}\text{cm}^{-1}$) which gives solutions an intense red-purple color. This band is very similar to the strong absorptions at ca 500 nm which are common,⁴⁵ if not universal,⁴⁶ characteristic of d^1-d^1 dimers containing $[\text{Mo}^{\text{V}}_2\text{O}_3]^{4+}$ cores with linear oxo bridges, and can be assigned to promotion from the a_g non-bonding orbital in Figure 2 to the b_u anti-bonding orbital - a small energy gap

would be expected between these orbitals, consistent with the low energy of the absorption, and the transition would have considerable MLCT character which would account for the intensity of the absorption.

The validity of this interpretation of the electronic spectrum of 2^{2+} is supported by the observation that the closely related d^1-d^1 dimer $\{[Nb(\eta^5-C_5H_5)_2(Sn-Me_3)(\mu-O)]\}$, in which the metal centers are similarly spin paired through the linear oxo bridge, is described as forming an "intensely blue solution", consistent with the presence of similar intense absorptions in the visible.³⁰ In sharp but not surprising contrast the closely related d^0-d^0 dimer of niobium $[Nb(\eta^5-C_5H_5)_2Cl]_2(\mu-O)[BF_4]_2$ is orange,^{27m} while most of the group 4 d^0-d^0 dimers in Table VI are colorless.

Photodisproportionation of $\{[W(\eta^5-C_5H_5)_2(CH_3)_2(\mu-O)] [PF_6]\}$. The bridging oxo dimer 2^{2+} is quite photosensitive, and the purple color of a solution of $2[PF_6]$ in acetonitrile was discharged and replaced with a pale orange color after ca 1.5 hours irradiation with a sunlamp. A 1H NMR spectrum of the solid obtained from such a reaction (acetone- d_6) contained singlet resonances of equal intensity in the cyclopentadienyl region at δ 6.90 and 5.38, together with two new methyl peaks at δ x and 0.36 with satellites indicating that they are bonded to W (^{183}W , $I = 1/2$, 14% abundance) and a resonance at δ 2.86 assigned to coordinated acetonitrile. This spectrum suggested that 2^{2+} had undergone the photodisproportionation reaction shown in Scheme II to give the novel terminal oxo complex $[W(\eta^5-C_5H_5)(O)(CH_3)]^+$ (3^+) and the tungstenocene methyl complex $[W(\eta^5-C_5H_5)_2(CH_3)]^+$,⁴⁷ trapped by the coordinating solvent acetonitrile as the 18-electron complex $[W(\eta^5-C_5H_5)_2(NCCH_3)(CH_3)]^+$ (4^+).

It is well established that many of the d^1-d^1 oxo bridged dimers containing $[MoV_2O_3]^{4+}$ cores participate in facile thermal disproportionation equilibria which give d^0 and d^2 monomers containing $[Mo^VI O_2]^{2+}$ and $[Mo^{IV} O]^{2+}$ cores,^{45,48} and we have recently reported that at least two examples of such molecules, the dithiocarbamate complex $[Mo_2O_3\{S_2CN(CH_2Ph)_2\}_4]$ (**5**) and its tungsten analog **6**, exhibit marked photochromism because the disproportionation

equilibria can be accessed both thermally and photochemically - irradiation of **5** and **6** induces disproportionation which is then reversed thermally (Scheme III).^{33b}

The photodisproportionation in Scheme II provides an intriguing complement to reactions such as those shown in Scheme III, since the tungstenocene complex **2**²⁺ provides the first example in which disproportionation of a d¹-d¹ dimer with a linear oxo bridge can be photochemically induced but is not observed thermally at room temperature. We therefore attempted independent syntheses of the proposed photodisproportionation products **3**⁺ and **4**⁺ to confirm their identity, and, following successful syntheses as described below, were able to confirm the hypothesis in Scheme II by comparison of the NMR characteristics of the pure complexes with those of the materials formed by photolysis of **2**²⁺.

Synthesis of the Acetonitrile Methyl Cation [W(η^5 -C₅H₅)₂(NCCH₃)(CH₃)]⁺. It has been known since 1979 that metal mono-methyl tungstenocene complexes such as the benzoate [W(η^5 -C₅H₅)₂{OC(O)Ph}(CH₃)] can be prepared by treatment of the dimethyl complex [W(η^5 -C₅H₅)₂(CH₃)₂] (**7**) with a protonic acid (benzoic acid in this case), in a sequence which presumably involves protolytic removal of one of the methyl groups as methane.²² We have been able to extend this approach to the synthesis of the acetonitrile methyl cation [W(η^5 -C₅H₅)₂(NCCH₃)(CH₃)]⁺ (**4**⁺) by reacting **7** with [NH₄]PF₆ in acetonitrile (Scheme I). The ammonium ion is a strong enough acid to protonate **7**, and in the absence of a coordinating anion like benzoate the 16-electron "[W(η^5 -C₅H₅)₂(CH₃)]⁺"⁴⁷ cation is trapped by the coordinating solvent as **4**⁺. This cation was isolated as the hexafluorophosphate salt **4** PF₆ in 70% yield and fully characterized by combustion analysis and spectroscopy as described in the Experimental Section. Comparison of the NMR characteristics of **4**⁺ with those of a solution of **2**[PF₆] in CD₃CN following photolysis confirmed that the higher field cyclopentadienyl and methyl resonances in the photolysed solution had been correctly assigned to **4**⁺.

Synthesis and Structural Characterization of the d^0 Oxo-Methyl Cation $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]^+$. The acetonitrile ligand in the complex 4^+ is substitutionally labile both thermally and photochemically, so that 4^+ is a convenient starting material for a number of tungstenocene methyl complexes of the $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{X}]$ and $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{L}]^+$ types (X^- and L represent anionic and neutral two electron ligands respectively).⁴⁹ This led us to examine photolysis of 4^+ under O_2 , and we have observed that this provides a convenient route to the d^0 oxo methyl complex $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]^+$

Photolysis of 4^+ under O_2 was conveniently carried out in acetone, and after ca one hour irradiation with a sunlamp the orange color of 4^+ had been discharged from a solution of 4PF_6 and replaced by a pale yellow color. Filtration and removal of the solvent gave spectroscopically pure yellow crystalline flakes, which could be recrystallized as lemon yellow flakes by slow concentration of a saturated acetone/toluene solution under reduced pressure. Combustion analysis was consistent with a $\text{C}_{11}\text{H}_{13}\text{WOPF}_6$ stoichiometry, and a ^1H NMR spectrum in CD_3CN contained resonances at δ 6.58 and δ 2.16, both with tungsten satellites, which integrated as 10 and 3 protons respectively, consistent with the presence of a complex containing a $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)]$ moiety. The complex was insoluble in aromatic and ethereal solvents, and the presence of the characteristic IR absorptions of PF_6^- confirmed that the compound was a salt.

The spectroscopic and analytical data were consistent with formulation of the oxidation product as the terminal-oxo methyl complex $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]\text{PF}_6$ (3PF_6), but it was not feasible on the basis of the available spectroscopic data to rule out formulation of the product as a dimer with a double oxo bridge: $[\{W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)(\mu\text{-O})\}_2]^{2+}$. Either formulation would account for the stoichiometry of the complex, and there is literature precedent for double oxo bridges between d^0 metal centers.⁵⁰ This ambiguity led us to attempt to characterize the complex crystallographically, but initial efforts were frustrated by the high solubility of the complex in polar solvents, which rendered unsuccessful attempts to grow diffraction quality crystals of the PF_6^- salt via layer diffusion, vapor diffusion, or low temperature recrystallization.

The crystallization problems were circumvented by exchange of I^- for the PF_6^- counterion to give a salt of 3^+ with reduced solubility in polar non-aqueous solvents. The exchange was carried out by addition of a 0°C solution of $3PF_6$ in acetone to a 0°C solution of NaI in acetone to precipitate **3I** as golden crystalline flakes. IR spectra of these flakes suggested that the desired exchange reaction had probably occurred, since the absorption bands characteristic of the PF_6^- anion were not observed, while the presence of a relatively strong and sharp band at 867 cm^{-1} (previously masked by the 840 cm^{-1} absorption of PF_6^-) was consistent with the presence of a terminal tungsten-oxo bond within the exchanged complex¹ - this is somewhat below the $900\text{--}1100\text{ cm}^{-1}$ range usually cited for terminal metal oxo groups,⁵¹ but is similar to the value of $789\text{--}879\text{ cm}^{-1}$ previously reported for the $W=O$ stretch in $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})]$.⁵² ^1H and ^{13}C NMR spectra of the flakes confirmed that the tungstenocene cation had remained intact during the anion exchange.

Bright yellow cubes of **3I** suitable for a diffraction study were obtained via vapor diffusion of diethyl ether into a saturated acetone solution, and a single crystal X-ray diffraction was used to characterize one of the cubes structurally as described in the Experimental Section. The displacement coefficients for the C and O atoms in the structure are somewhat high, limiting the precision of the derived bond lengths and angles, but the diffraction study does unambiguously establish that **3I** does indeed contain the terminal oxo alkyl complex $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]^+$ as the discrete, monomeric cation illustrated in Figure 4 and characterized by the bond lengths and angles in Tables VII and VIII.

The niobocene complex isoelectronic with 3^+ , $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]$, is known,⁵³ together with the related complexes $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{O})\text{X}]$ ($\text{X} = \text{Cl}, \alpha\text{-C}_4\text{H}_3\text{S}, \alpha\text{-CH}_2\text{C}_5\text{H}_4\text{N}$),⁵⁴ and the pentamethyl tungstenocene analog $[W(\eta^5\text{-C}_5\text{Me}_5)(\text{O})(\text{CH}_3)]^+$ ⁵⁵ but $[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{O})(\text{CH}_3)]$,⁵⁶ $[\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2(\text{O})]$,⁵⁷ and $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{O})\text{H}]$ ⁵⁸ are the only other crystallographically characterized terminal-oxo complex of metallocenes.

The 3^+ cation contains a pseudotetrahedral arrangement of two η^5 -cyclopentadienyl rings, a terminally bound oxygen atom, and a methyl group bound to a central tungsten atom. If

the two ring centroids, the oxygen atom, and the methyl carbon atom are used to determine a distorted tetrahedron, the angles about W display a maximum and minimum deviation from the tetrahedral value (109°) of 20° and 2° , respectively (see Table VIII).

The tungsten-cyclopentadienyl carbon bond distances are not all equal within experimental error: the distances become progressively longer as one moves around the rings away from the terminal-oxo ligand. The difference between the longest (W-C(13)) and the shortest (W-C(15)) distance within Cp(1) is 0.186 (26) Å; the difference between the longest (W-C(25)) and the shortest (W-C(24)) distance within Cp(2) is 0.166 (29) Å. The average values of the tungsten-cyclopentadienyl carbon bond distances (2.375 (9) Å for Cp(1) and 2.368 (9) Å for Cp(2)) lie just outside the 2.26 - 2.35 Å range typically observed for the analogous values in other $[\text{W}(\eta^5\text{-C}_5\text{H}_5)]$ containing complexes.²⁷

The cyclopentadienyl rings within the structure are tilted slightly away from perfect η^5 bonding, as manifested in values for the angles between the ring normals and the corresponding tungsten ring centroid vectors of 5.3° for Cp(1) and 1.2° for Cp(2). The origin and significance of this tilt is, however, unclear, given the level of precision of the present crystallographic study. The perpendicular distances from the cyclopentadienyl mean ring planes to the tungsten atoms (2.067 Å for Cp(1) and 2.049 Å for Cp(2)) and the angle between the ring normals (52.6°) lie somewhat outside the 1.93 - 2.01 Å and $34 - 49^\circ$ ranges, respectively, observed for the analogous values in other tungstenocene complexes.²⁷ The dihedral angle between the plane defined by the two ring centroids and W and the plane defined by C(1), W, and O(1) is 88.4° , a value consistent with the pseudo-tetrahedral structure of the cation.

The $\text{W}^{\text{VI}}\text{-CH}_3$ σ bond length of 2.219 (16) Å is slightly shorter, as would be expected, than the value of 2.227 (8) Å established above for the $\text{W}^{\text{V}}\text{-CH}_3$ σ bond in 2^{2+} and noticeably shorter than the values of 2.25 (2) and 2.25 (2) Å in the literature for $\text{W}^{\text{IV}}\text{-C}$ σ bonds in tungstenocene alkyls such as $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{C}_6\text{H}_3\text{Me}_2)_2]^{27g}$ and $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{CH}_2\text{PMe}_2\text{Ph})\text{-(CH}_3)]^+$.^{27f} The $\text{W}^{\text{VI}}\text{-CH}_3$ bond in 3^+ is, however, somewhat longer

than W^{VI} -alkyl σ bonds in some other ligand environments such as that in $[W_2O_3(CH_2CMe_3)_6]$ (2.134 (8) Å).⁵⁹

The W-O(1) bond distance of 1.700 (11) Å falls within the 1.66 - 1.73 Å range observed for the M=O bond distances in d^0 and d^1 complexes of Mo and W (the ionic radii of these two metals are essentially identical in both oxidation states²⁹). The C(1)-W-O(1) bond angle of 93.8 (7)° falls just within the 93 - 98° range observed for the XMX angle in d^0 bent metallocene complexes.²⁷

With **3I** fully characterized structurally and spectroscopically we were able to confirm by comparison with the 1H NMR spectra of an isolated sample that the lower field cyclopentadienyl and methyl resonances in the solution formed by photolysis of **2²⁺** in CH_3CN had been correctly assigned to **3⁺**, and that Scheme II does describe the photolysis reaction.

Mechanism of the Oxidation of $[W(\eta^5-C_5H_5)_2(NCCH_3)(CH_3)]^+$ to $[W(\eta^5-C_5H_5)_2(O)(CH_3)]^+$. It was clear from the reaction conditions that molecular oxygen was the source of the oxo ligand in **3⁺**, and **3⁺** could not be formed from **4⁺** in the absence of oxygen or air. We also examined the reaction of **4⁺** with excess water under nitrogen in acetone - only traces of **2²⁺** were formed when this mixture was gently heated, and formation of **3⁺** was not observed.

Deliberate irradiation is not essential for the oxidation of **4⁺** to **3⁺**, and the reaction typically proceeds in good yield when a solution of **4PF₆** in acetone is stirred under air or oxygen for a day. The reaction is, however, less reproducible under these conditions (possibly as a consequence of variations in laboratory illumination), and use of a sunlamp is recommended to allow a more convenient reaction time and to ensure reproducibility. Irradiation of **4⁺** most probably induces dissociation of the acetonitrile ligand and generates coordinatively unsaturated $[W(\eta^5-C_5H_5)_2(CH_3)]^+$,⁴⁷ which can complex molecular oxygen (Scheme IV). Details of subsequent steps in the formation of **3⁺** have not been established, but the most reasonable possibility, as shown in the Scheme, is one in which the O_2 adduct is an 18-electron peroxide

complex 8^+ and peroxo cleavage is induced by coordination of a second "[W(η^5 -C₅H₅)₂(CH₃)]⁺" (9^+) fragment. Direct experimental support for this mechanism is lacking, but strong circumstantial support is provided by the report of the structural characterization of [Nb(η^5 -C₅H₅)₂(η^2 -O₂)Cl], isoelectronic with 8^+ , as an η^2 -peroxo complex.⁶⁰

If the role of 4^+ is solely that of a source of 9^+ we should be able to prepare 3^+ from other 9^+ sources. We have confirmed that this is indeed the case, most intriguingly in the present system by examining the photolysis of the bridging oxo complex 2^{2+} in acetone. Under nitrogen this gave a complex mixture of tungstenocene derivatives, including 3^+ , [W(η^5 -C₅H₅)₂(C₂H₄)H]⁺, and at least five other tungstenocene derivatives (¹H NMR). Under air, however, the purple color of 2^{2+} was rapidly replaced by a pale yellow color and ¹H NMR analysis indicated essentially quantitative comparison to 3^+ , consistent with photochemical disproportionation of 2^{2+} to a mixture of 3^+ and 9^+ and subsequent oxidation of the 9^+ to 3^+ by molecular oxygen.

Mechanism of the Oxidation of [W(η^5 -C₅H₅)₂(OCH₃)(CH₃)] to [W(η^5 -C₅H₅)₂(CH₃)₂(μ -O)]²⁺ in MEK and Oxidation of [W(η^5 -C₅H₅)₂(OCH₃)(CH₃)] under Anhydrous Conditions. The origin of the bridging oxo group in 2^{2+} is the most intriguing of the mechanistic questions posed by the oxidation of **1** to 2^{2+} , but is one to which we do not have a definitive answer. It seems unlikely that adventitious oxygen is the source, since the reaction proceeds reliably in good yield under anoxic conditions, and this leaves the oxygen of the methoxy ligand in **1** or a trace of water in the ketonic solvent as the most probable sources of the oxygen atom. A definitive distinction between these possibilities would require an oxygen labelling study which we have not carried out, but there are several observations which limit the possibilities.

A strong argument in favor of an important role for adventitious water in the formation of 2^{2+} is provided by the observation that room temperature ferrocenium oxidation of **1** in CH₂Cl₂, a solvent which can be rendered essentially anhydrous, does not give 2^+ but instead leads to only

small quantities of diamagnetic products, as determined by quantitative ^1H NMR (CD_3CN , $^t\text{BuOH}$ as internal standard) corresponding to a 12% yield of $\mathbf{3}^+$ and a 6% yield of another tungstenocene complex tentatively identified as the formaldehyde complex $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-CH}_2=\text{O})(\text{CH}_3)]^+$ ($\mathbf{10}^+$).

The major product of the CH_2Cl_2 oxidation is a paramagnetic complex with an EPR signal with quartet hyperfine structure ($a = 4.0$ G) indicative of the presence of a methyl group, and an isotropic g value of 2.006 intermediate between the typical values observed for 17-electron dihalo^{24b} and dialkyl^{25b} tungstenocene derivatives. A number of paramagnetic tungstenocene complexes of the general type $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2\text{XY}]^+$ have been reported, but it is unusual to observe resolved hyperfine coupling to the X or Y ligands,^{24b} and this distinctive hyperfine "finger print" enables us to assign the EPR resonance unambiguously to $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}]^+$ ($\mathbf{11}^+$), a previously unknown tungstenocene radical which we have been able to prepare independently from $\mathbf{7}$ as shown in Scheme I.

The first step in the independent preparation of $\mathbf{11}^+$ involves a variation on the conversion of $\mathbf{7}$ to $\mathbf{4}^+$ by ammonium ion protolysis in which the use of NH_4Cl leads to the formation of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}]$ ($\mathbf{12}$), following coordination of the chloride counterion to intermediate $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)]^+$. The methyl chloride complex $\mathbf{12}$ was characterized spectroscopically and analytically as described in the Experimental Section and was conveniently oxidized with ferrocenium to the radical cation $\mathbf{11}^+$ in excellent yield. The paramagnetism of $\mathbf{11}^+$ limited the spectroscopic tools available for its characterization, but in addition to combustion analysis and EPR data our formulation of $\mathbf{11PF}_6$ as $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\text{Cl}]\text{PF}_6$ is strongly supported by reduction of the salt back to $\mathbf{12}$ in 50% yield using the KOH /acetone mixture which we have previously found to be a convenient reductant in the tungstenocene system.²⁵

The tentative characterization of $\mathbf{10}^+$ as a formaldehyde complex is supported by the observation of similar signals in ^1H NMR spectra of material prepared by reaction of $\mathbf{4}^+$ (as a

convenient source of 9^+) with paraformaldehyde, but we have been unable to date to obtain pure samples of $10PF_6$ from this or other preparative approaches.

The failure to form 2^{2+} when **1** is oxidized in CH_2Cl_2 would be a convincing argument against the possibility that the bridging oxo group in 2^{2+} can originate from the methoxy ligand except for the curious observation that a significant yield of 2^{2+} was obtained (53% by quantitative 1H NMR together with 10% 3^+) when the ferrocenium oxidation of **1** in CH_2Cl_2 was carried out at $-78^\circ C$. The course of this reaction was, however, visually complex - the material obtained after $-78^\circ C$ oxidation and solvent removal at $-45^\circ C$ was brown and did not acquire the characteristic purple of 2^+ until it had been dried under vacuum.

It is clear that the available information does not allow us to establish definitely the mechanisms by which 2^{2+} and 11^+ are formed from **1** in MEK and CH_2Cl_2 respectively, and that the reaction sequences must involve a number of steps beyond those established to date. In the case of the MEK oxidation, for example, it seems probable (Scheme V) that initial oxidation of **1** is followed by loss of a methoxy radical and formation of an intermediate aquo complex, but conversion of this to 2^{2+} must be more complex than a simple condensation. One possibility is that hydrogen atom loss for the aquo complex generates a 17 electron hydroxy complex which forms 2^{2+} by condensation, and the proposal of an intermediate hydroxy complex is supported by the analogy between the condensation step in Scheme V and that monitored by Doppert when he established that $[Ti(\eta^5-C_5H_5)_2(OH_2)]_2(\mu-O)^{2+}$ is formed by condensation of $[Ti(\eta^5-C_5H_5)_2(OH_2)OH]^+$.^{61,62}

Formation of 11^+ by oxidation of **1** in CH_2Cl_2 must be similarly complex - it is reasonable, particularly in light of the recent establishment of a number of classes of halocarbon complexes,⁶³ that a CH_2Cl_2 complex such as $[W(\eta^5-C_5H_5)_2(Cl_2CH_2)]^+$ is an intermediate in the reaction (Scheme VI), but subsequent conversion to 11^+ must involve at least one further homolysis.

The sequences in Schemes V and VI involve several radical intermediates and must be regarded as speculative, but it is difficult to envisage simpler alternatives unless a methoxide ion

dissociates from the initially formed $[W(\eta^5-C_5H_5)_2(OCH_3)(CH_3)]^+$ to give an exceptionally electrophilic and completely unprecedented 15-electron dicationic W(V) complex " $[W(\eta^5-C_5H_5)_2(CH_3)]^{+2}$ ". We conclude that the reaction sequences are complex, and that **2**²⁺ and **11**⁺ may be formed from **1** by more than one pathway.

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Supplementary Material Available: Tables S-I and S-II, anisotropic displacement coefficients for **2**[PF₆]₂ and **3I**; Tables S-III and S-IV calculated hydrogen atom parameters for **2**[PF₆]₂ and **3I** (x pages, ordering information is given on any current masthead page).

Figure 1. Molecular structure of $[\{W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})]^{2+}$ (50% probability ellipsoids).

Figure 2. Frontier orbitals of $[\{W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})]^{2+}$.

Figure 3. Electronic spectrum of 1.2×10^{-4} mole L^{-1} solution of $[\{W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)\}_2(\mu\text{-O})][\text{PF}_6]$ in CH_3CN .

Figure 4. Molecular structure of the $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]^+$ cation in **3l** (50% probability ellipsoids).

Table I. Summary of Crystallographic data for $[\{W(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2(\mu\text{-O})\}[\text{PF}_6]_2$ (**2** $[\text{PF}_6]_2$) and $[W(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]\text{I}$ (**3****I**).

Crystal Data		
	2 $[\text{PF}_6]_2$	3 I
color	dark red-purple	bright yellow
shape	hexagonal plates	cubes
dimensions (mm)	0.10 x 0.20 x 0.50	0.30 x 0.30 x 0.30
formula	$\text{C}_{22}\text{H}_{26}\text{F}_{12}\text{OP}_2\text{W}_2$	$\text{C}_{11}\text{H}_{13}\text{IOW}$
crystal system	monoclinic	cubic
space group	$\text{P}2_1/\text{c}$	$\text{Ia}3$
a (Å)	7.246(3)	24.601(4)
b (Å)	18.796(6)	24.601(4)
c (Å)	9.438(4)	24.601(4)
β (deg)	89.98(2)	90
V (Å ³)	1285(3)	14889(4)
Z	2	48
d_c (g/mL)	2.49	2.53
μ (cm ⁻¹)	93.6	119.4
T (°C)	23	23

Data Collection

λ (Å)	0.71073	0.71073
scan type	2 θ : θ	2 θ : θ
max. 2 θ (deg)		60
min. 2 θ (deg)	3.5	3.5
scan speed (deg/min)	variable, 3-15	variable, 3-15
data collected	$\pm h, +k, +l$	$+h, +k, +l$
unique data	1661 (2159 read)	2216 (8310 read)
unique data observed $F_o > 2.5\sigma(F_o)$	1663 with $F_o > 3\sigma(F_o)$	1768 with
std reflns	3/63	3/63

Agreement Factors

R_F (%) ^a	3.13	6.52
wR_F (%) ^b	3.09	6.03
max residue peak (eÅ ⁻³)	0.44	0.53
weighting factor, g	0.0008	0.0008

$$^a R_F = \sum |F_{\text{obsd}} - F_{\text{calcd}}| / \sum |F_{\text{obsd}}|$$

$$^b wR_F = \sum [(w)^{1/2} (F_{\text{obsd}} - F_{\text{calcd}})] / \sum [(w)^{1/2} F_{\text{obsd}}]$$

Table II. Fractional Atomic Coordinates ($\times 10^4$) for $[(W(\eta^5-C_5H_5)_2(CH_3))_2(\mu-O)] [PF_6]_2$.

Atom	X/A	Y/B	Z/C
W(1)	4707.0 (4)	4245.7 (1)	1327.1 (3)
C(1)	1703 (11)	4451 (5)	1043 (10)
O(1)	5000 (0)	5000 (0)	0000 (0)
C(11)	4358 (17)	2988 (4)	1443 (14)
C(12)	6213 (14)	3140 (5)	1272 (15)
C(13)	6519 (14)	3479 (6)	12 (12)
C(14)	4762 (14)	3507 (4)	-675 (8)
C(15)	3495 (13)	3208 (5)	184 (10)
C(21)	6698 (13)	4315 (6)	3262 (8)
C(22)	6287 (16)	5001 (6)	2841 (7)
C(23)	4406 (11)	5111 (5)	3070 (7)
C(24)	3673 (11)	4513 (5)	3621 (9)
C(25)	5171 (14)	3966 (5)	3781 (8)
P(1)	-16 (2)	1593 (1)	1241 (2)
F(1)	-2198 (6)	1619 (3)	1331 (10)
F(2)	2166 (6)	1557 (3)	1166 (9)
F(3)	-143 (8)	796 (3)	723 (6)
F(4)	107 (7)	2384 (3)	1767 (6)
F(5)	75 (11)	1323 (4)	2804 (5)
F(6)	-118 (13)	1858 (4)	-315 (5)

Table III. Fractional Atomic Coordinates ($\times 10^4$) for $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]\text{I}$.

Atom	X/A	Y/B	Z/C
W	1553.0 (3)	6136.6 (2)	1311.7 (3)
I(1)	2500 (0)	2500 (0)	2500 (0)
I(2)	2500 (0)	4810 (1)	0 (0)
I(3)	1187 (1)	1187 (1)	1187 (1)
O(1)	1089 (5)	6509 (5)	1664 (5)
C(1)	928 (7)	5622 (7)	914 (9)
C(11)	1573 (10)	5607 (11)	2124 (11)
C(12)	1607 (12)	5262 (9)	1734 (13)
C(13)	2056 (13)	5282 (10)	1463 (9)
C(14)	2361 (8)	5749 (16)	1645 (14)
C(15)	2016 (11)	5921 (9)	2085 (9)
C(21)	1752 (13)	6225 (11)	359 (10)
C(22)	1415 (9)	6743 (13)	568 (10)
C(23)	1818 (10)	6977 (8)	908 (9)
C(24)	2213 (9)	6674 (8)	977 (13)
C(25)	2237 (11)	6246 (9)	614 (9)

Table IV. Bond Lengths (Å) within $[\{W(\eta^5-C_5H_5)_2(CH_3)\}_2(\mu-O)]^{2+}$.

W(1)-C(1)	2.227 (8)	C(11)-C(12)	1.383 (14)
W(1)-O(1)	1.904 (0)	C(12)-C(13)	1.367 (15)
W(1)-C(11)	2.379 (8)	C(13)-C(14)	1.430 (13)
W(1)-C(12)	2.349 (9)	C(14)-C(15)	1.348 (11)
W(1)-C(13)	2.311 (9)	C(15)-C(11)	1.404 (14)
W(1)-C(14)	2.345 (7)	C(21)-C(22)	1.382 (14)
W(1)-C(15)	2.396 (8)	C(22)-C(23)	1.395 (12)
W(1)-C(21)	2.331 (8)	C(23)-C(24)	1.347 (12)
W(1)-C(22)	2.317 (9)	C(24)-C(25)	1.503 (13)
W(1)-C(23)	2.323 (8)	C(25)-C(11)	1.376 (13)
W(1)-C(24)	2.345 (8)		
W(1)-C(25)	2.399 (7)		

Table V. Bond Angles (deg) within $[\{W(\eta^5-C_5H_5)_2(CH_3)\}_2(\mu-O)]^{2+}$.

C(11)-C(12)-C(13)	111 (1)	C(21)-C(22)-C(23)	108 (1)
C(12)-C(13)-C(14)	106 (1)	C(22)-C(23)-C(24)	109 (1)
C(13)-C(14)-C(15)	109 (1)	C(23)-C(24)-C(25)	109 (1)
C(14)-C(15)-C(11)	109 (1)	C(24)-C(25)-C(21)	103 (1)
C(15)-C(11)-C(12)	106 (1)	C(25)-C(21)-C(22)	112 (1)
C(1)-W(1)-O(1)	84.3 (3)	W(1)-O(1)-W(1A)	180 (0)
Cp(1) ^a -W(1)-Cp(2) ^b	129.5		
Cp(1)-W(1)-C(1)	103.5		
Cp(1)-W(1)-O(1)	113.0		
Cp(2)-W(1)-C(1)	104.3		
Cp(2)-W(1)-O(1)	111.0		

^aCp(1) is the centroid of the cyclopentadienyl ligand containing C(11)-C(15).

^bCp(2) is the centroid of the cyclopentadienyl ligand containing C(21)-C(25).

Table VI. Selected Molecular Parameters for Bridging-Oxo Metallocene Complexes of the Type $\{M(\eta^5-C_5H_5)_2X\}_2(\mu-O)^{n+}$ ($n = 0, 2$).

Complex	Electron Count	M-O-M' Angle	Dihedral Angle ^a	M-O Bond Length
$\{Ti(\eta^5-C_5H_5)_2(OH_2)_2(\mu-O)[ClO_4]\}_2^{37}$	d ⁰ -d ⁰	175.8 (5)	74.1	1.829 (2)
$\{Ti(\eta^5-C_5H_5)_2(OH_2)_2(\mu-O)[S_2O_6]\}_2^{38}$	d ⁰ -d ⁰	177.0	74.1	1.834
$\{Ti(\eta^5-C_5H_5)_2Cl)_2(\mu-O)\}_2^{39}$	d ⁰ -d ⁰	173.8	75.4	1.837 (2)
$\{Ti(\eta^5-C_5H_5)_2(C\{CF_3\}H)_2(\mu-O)\}_2^{40}$	d ⁰ -d ⁰	170.0 (2)	53.9 (avg)	1.856 (6)
$\{Hf(\eta^5-C_5H_5)_2(CH_3)_2(\mu-O)\}_2^{41}$	d ⁰ -d ⁰	173.9 (3)	75.4	1.941 (3)
$\{Zr(\eta^5-C_5H_5)_2Cl)_2(\mu-O)\}_2^{42}$	d ⁰ -d ⁰	168.9 (8)	74.3	1.94 (1)
$\{Zr(\eta^5-C_5H_5)_2(CH_3)_2(\mu-O)\}_2^{43}$	d ⁰ -d ⁰	174.1 (3)	76.6	1.948 (1)
$\{Zr(\eta^5-C_5H_5)_2(SPh)_2(\mu-O)\}_2^{44}$	d ⁰ -d ⁰	165.8 (8)	61.7	1.966 (3) (avg)
$\{Nb(\eta^5-C_5H_5)_2Cl)_2(\mu-O)[BF_4]\}_2^{27m}$	d ⁰ -d ⁰	169.3 (8)	72.5	1.88 (1)
$\{Nb(\eta^5-C_5H_5)_2(C_4H_9)_2(\mu-O)\}_2^{45}$	d ¹ -d ¹	180	180	1.926 (2)
$\{Nb(\eta^5-C_5H_5)_2(SnMe_3)_2(\mu-O)\}_2^{40}$	d ¹ -d ¹	180	180	1.9434 (4)
$\{Nb(\eta^5-C_5H_4Me)_2Cl)_2(\mu-O)\}_2^{36}$	d ¹ -d ¹	180	180	

^aDefined as the angle between the X-M-O and X'-M'-O planes. A value of 0° would correspond to a syn orientation of the X and X' ligands.

Table VII. Bond Lengths (Å) within $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{O})(\text{CH}_3)]^+$

W-C(1)	2.219 (16)	C(11)-C(12)	1.285 (31)
W-O(1)	1.700 (11)	C(12)-C(13)	1.289 (31)
W-C(11)	2.386 (23)	C(13)-C(14)	1.442 (37)
W-C(12)	2.392 (20)	C(14)-C(15)	1.437 (34)
W-C(13)	2.467 (19)	C(15)-C(11)	1.338 (30)
W-C(14)	2.352 (21)	C(21)-C(22)	1.605 (34)
W-C(15)	2.280 (18)	C(22)-C(23)	1.419 (30)
W-C(21)	2.403 (20)	C(23)-C(24)	1.235 (26)
W-C(22)	2.385 (19)	C(24)-C(25)	1.382 (29)
W-C(23)	2.384 (19)	C(25)-C(21)	1.347 (29)
W-C(24)	2.250 (21)		
W-C(25)	2.418 (20)		

Table VIII. Bond Angles (deg) within $[\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{O})(\text{CH}_3)]^+$

C(11)-C(12)-C(13)	115 (3)	C(21)-C(22)-C(23)	99 (2)
C(12)-C(13)-C(14)	108 (2)	C(22)-C(23)-C(24)	113 (2)
C(13)-C(14)-C(15)	99 (2)	C(23)-C(24)-C(25)	114 (3)
C(14)-C(15)-C(11)	111 (2)	C(24)-C(25)-C(21)	107 (3)
C(15)-C(11)-C(12)	106 (3)	C(25)-C(21)-C(22)	106 (2)
C(1)-W-O(1)	93.8 (7)		
Cp(1) ^a -W-Cp(2) ^b	128.6		
Cp(1)-W-C(1)	100.2		
Cp(1)-W-O(1)	111.0		
Cp(2)-W-C(1)	104.2		
Cp(2)-W-O(1)	111.7		

^aCp(1) is the centroid of the cyclopentadienyl ligand containing C(11)-C(15)

^bCp(2) is the centroid of the cyclopentadienyl ligand containing C(21)-C(25)

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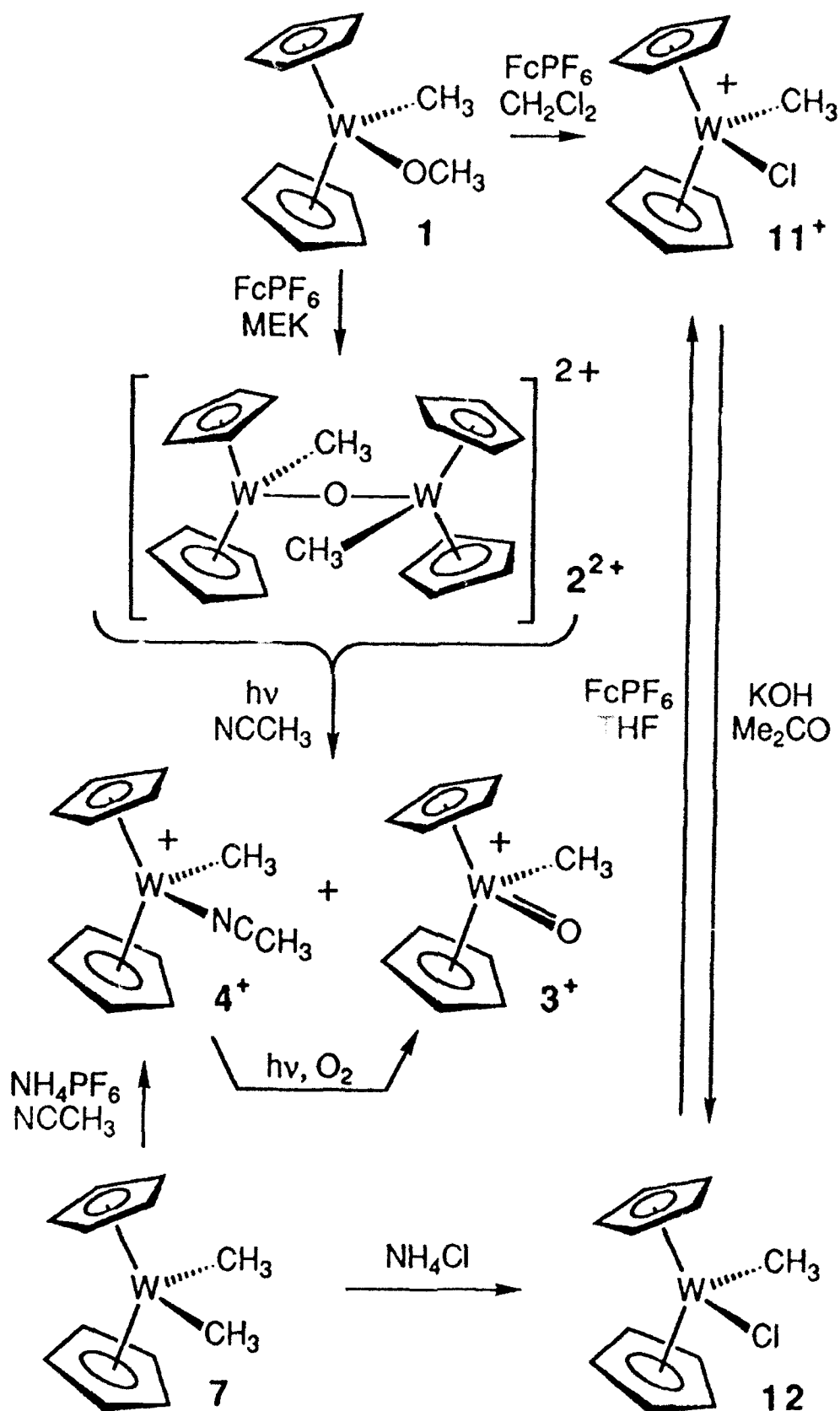
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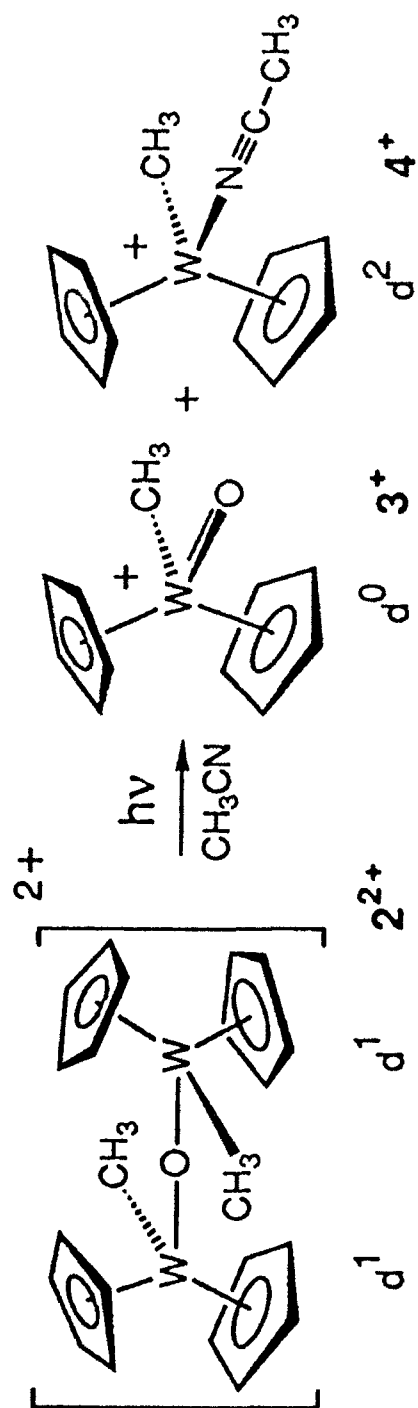
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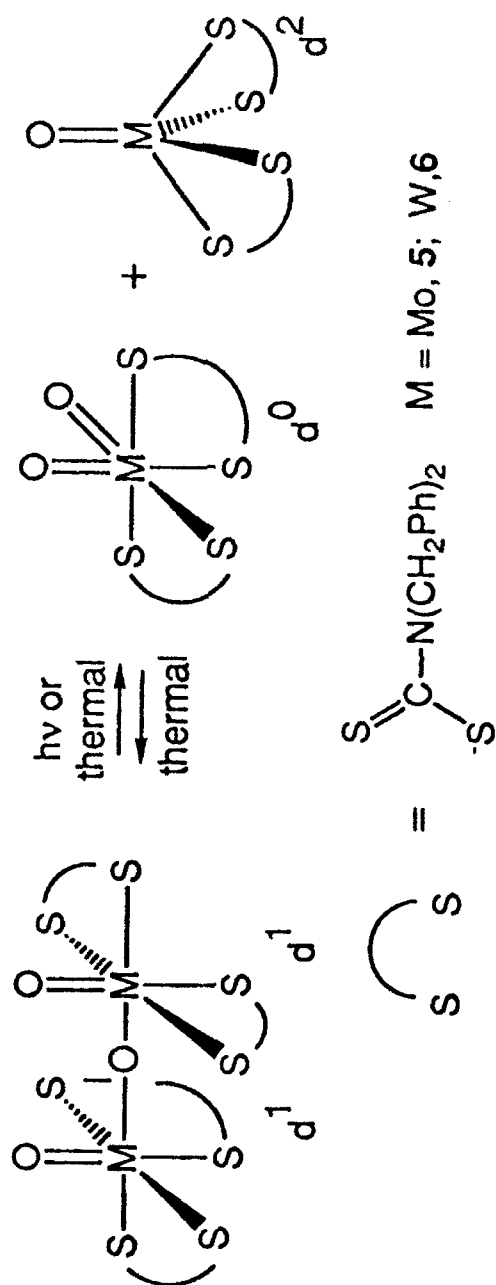
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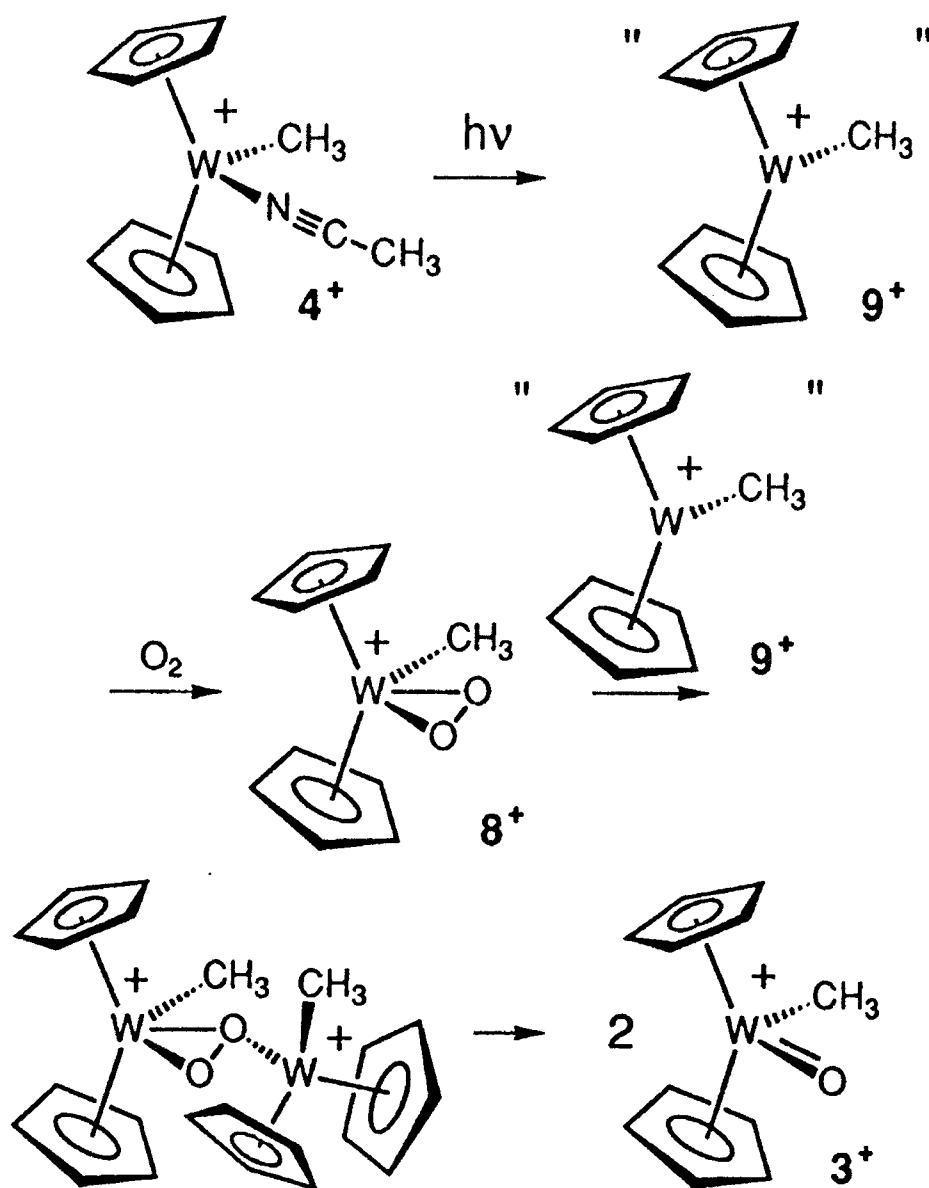
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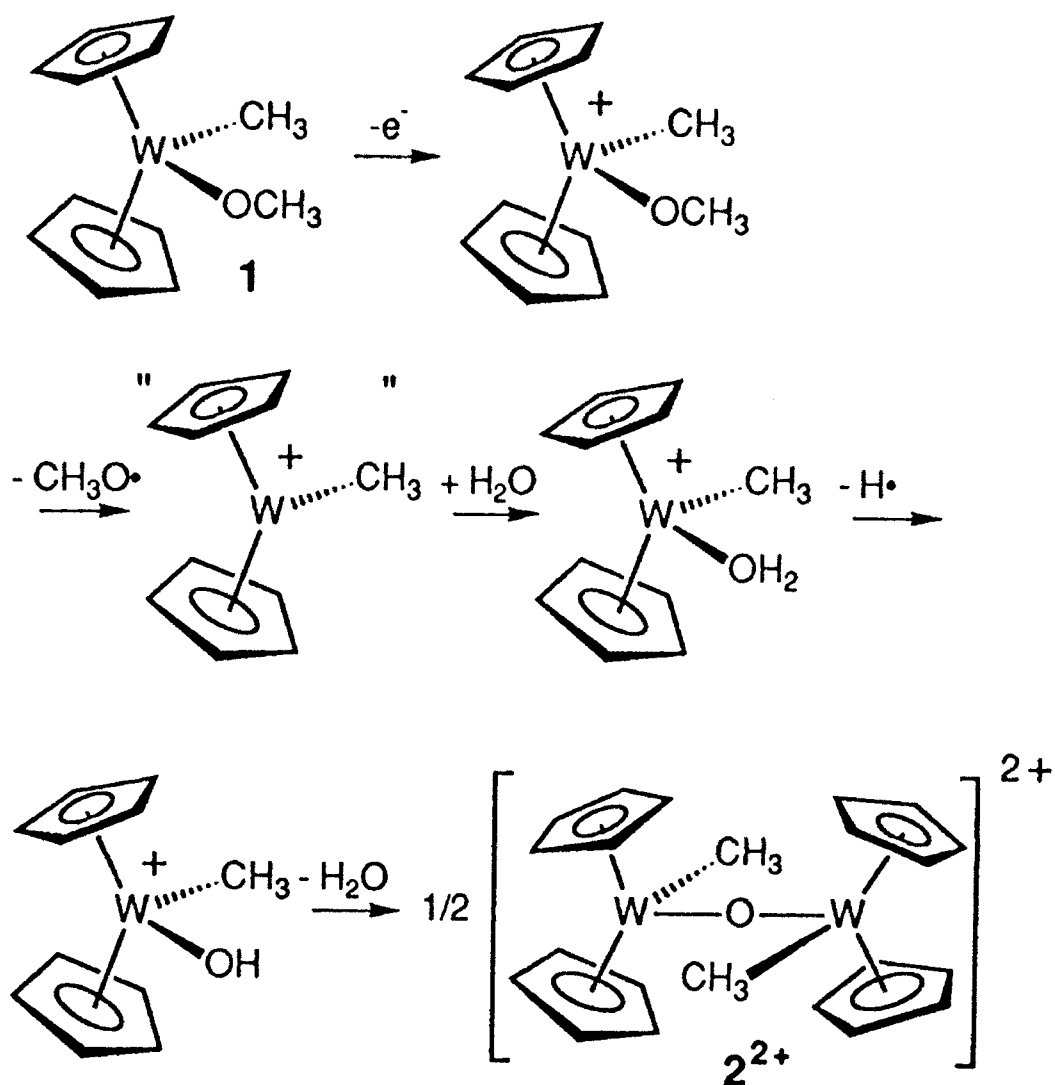
Scheme I

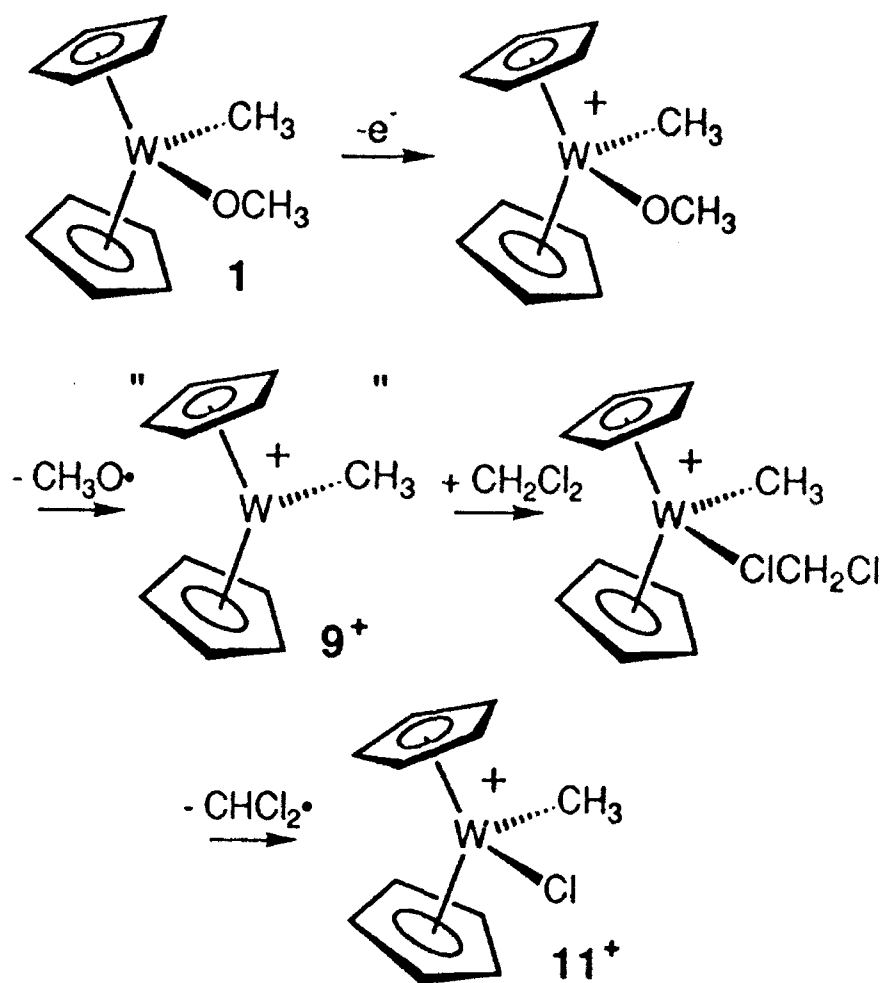






Scheme IV





Scheme VI

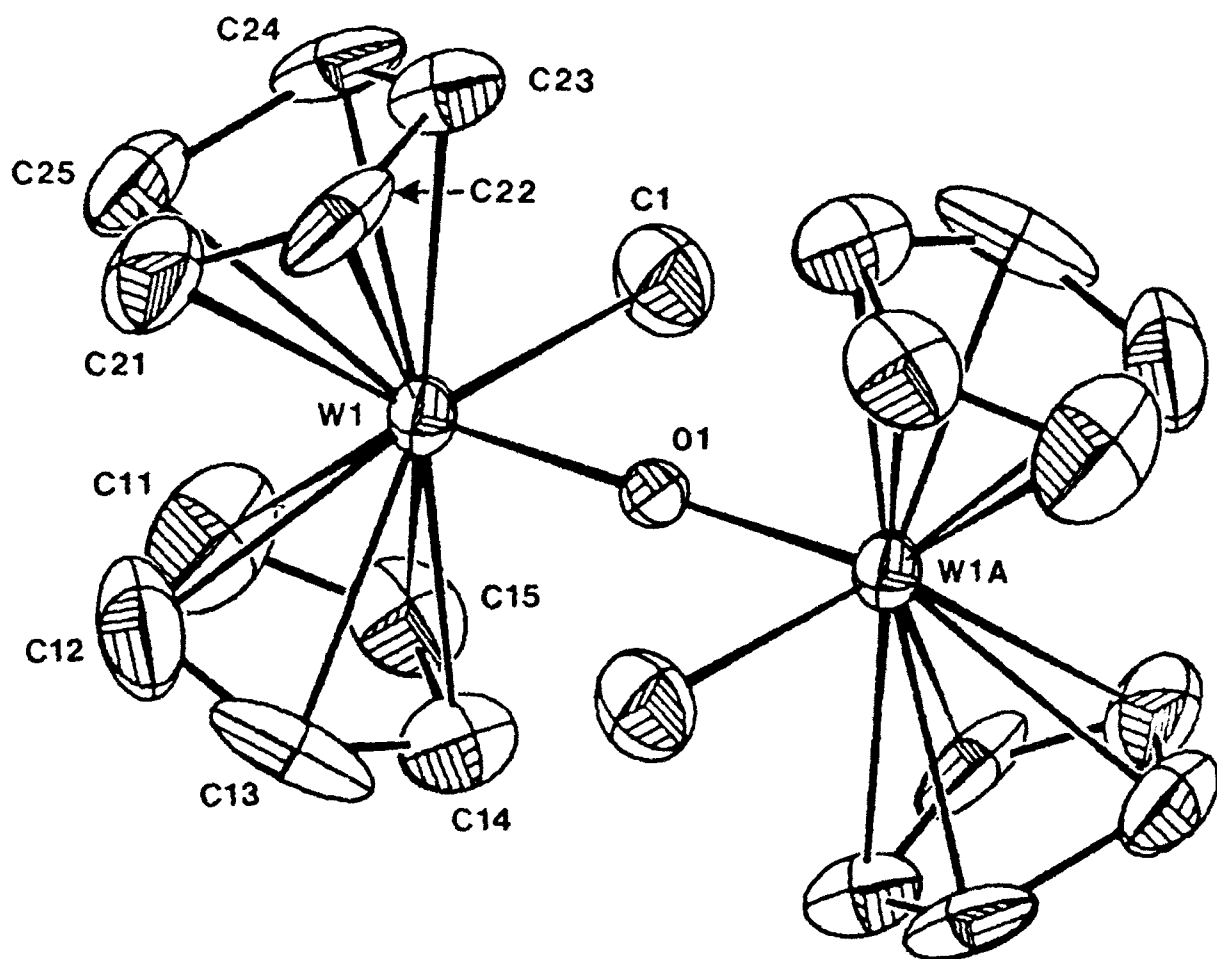


Figure 1

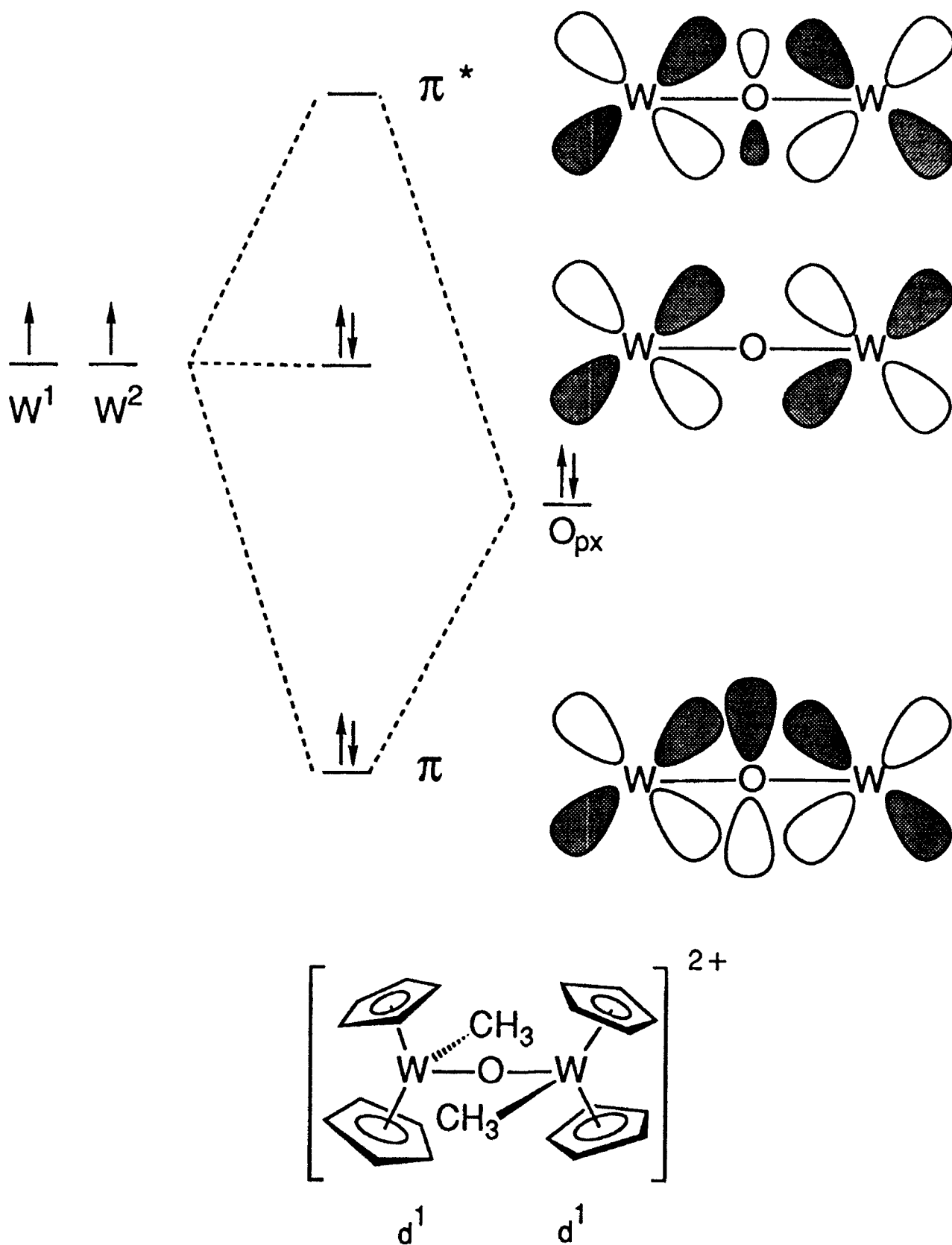


Figure 2

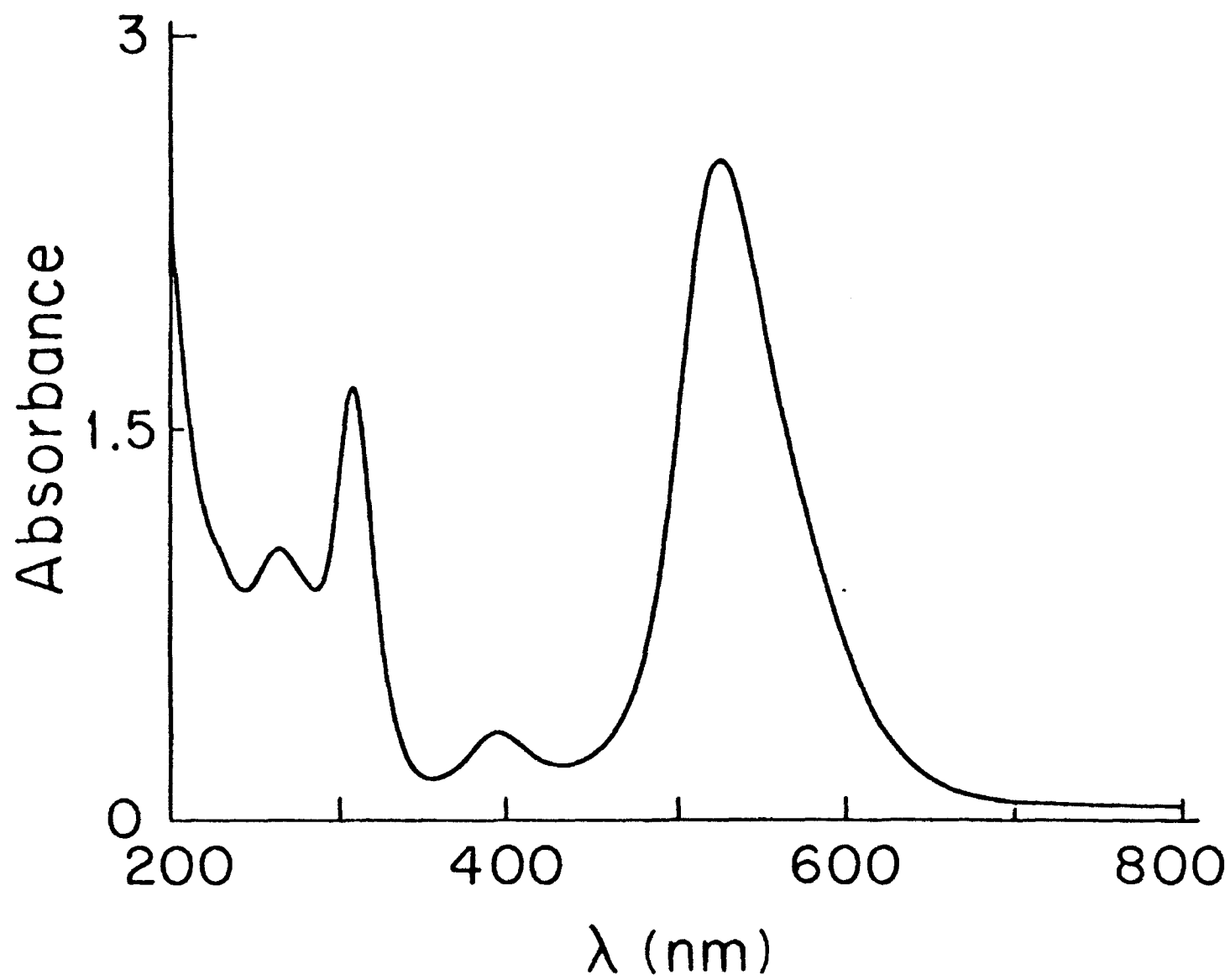


Figure 3

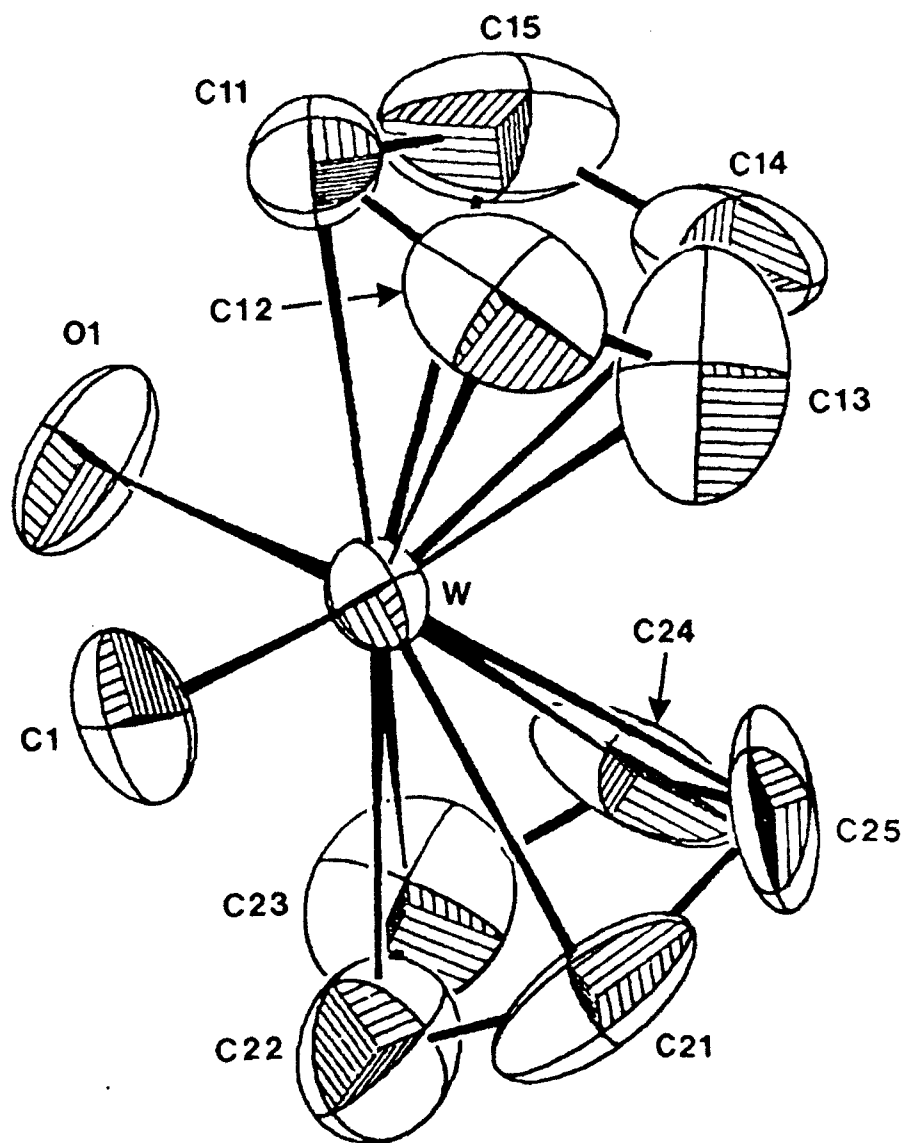


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